



**ATTACHMENT A**  
**Remarks**

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**NOV 20 2003**  
**TC 1700**

Claims 1 and 5-44 stand pending in the present application. By this Amendment, Applicants have amended claims 1, 6, 13, 21 and 37. Applicants respectfully submit that upon entrance of the present amendment, the present application will be placed in condition for allowance based on the discussion which follows.

Claim 37 was rejected under 35 U.S.C. § 112, second paragraph. By this Amendment, Applicants have corrected a typographical error thereby rendering the prior 35 U.S.C. § 112, second paragraph, rejection moot.

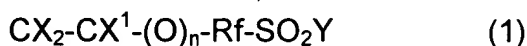
Claims 1, 5, 6, 7, 14, 15 and 16 were rejected under 35 U.S.C. § 102(b) as being anticipated by Masayuki et al (JP 06-260,184; hereinafter "Masayuki") and claims 1, 5, 6, 7, 14-21 and 41 were rejected under 35 U.S.C. § 102(b) as being anticipated by Harada (U.S. Patent No. 5,399,184). Claims 8-13, 22-40 and 42-44 were rejected under 35 U.S.C. § 103(a) as being unpatentable over Harada.

Contrary to the Examiner's allegation, the present invention is novel and not obvious in view of the prior art of record. Specifically, the present invention recites a novel and non-obvious material as provided below.

The present invention as recited in claim 1, relates to a material for a solid polyelectrolyte, comprising a multi-segmented fluoropolymer having:

a fluoropolymer chain segment A containing sulfonic acid functional groups,  
which is a copolymer comprising:

- (a) an ethylenic fluoromonomer unit containing sulfonic acid functional groups represented by Formula (1)



wherein X and X<sup>1</sup> may be the same or different and are each hydrogen or fluorine; Y is F, Cl or OY<sup>1</sup> wherein Y<sup>1</sup> is hydrogen, alkali metal or C<sub>1</sub> to C<sub>5</sub> alkyl; Rf is C<sub>1</sub> to C<sub>40</sub> divalent fluoroalkylene or C<sub>1</sub> to C<sub>40</sub> divalent fluoroalkylene having ether bond(s); and n is 0 or 1; and

- (b) at least one type of ethylenic fluoromonomer unit copolymerizable with the ethylenic fluoromonomer unit and containing no sulfonic acid functional groups;

and a fluoropolymer chain segment B containing no sulfonic acid functional groups, the fluoropolymer chain segment B having a crystalline melting point of 100°C or higher or a glass transition point of 100°C or higher.

In the present invention, the multi-segmented fluoropolymer is produced by combine a segment A with a segment B in the form of blocks or a graft as shown in Fig. 1 of the present specification (a copy of which is included in **Appendix 1** to this Amendment), where:

segment A : a random copolymer containing an ethylenic fluoromonomer unit containing sulfonic acid functional groups and an ethylenic fluoromonomer unit containing no sulfonic acid functional groups.

segment B : a polymer containing no sulfonic acid functional groups.

The present invention also relates to a material for a solid polyelectrolyte, comprising a multi-segmented fluoropolymer having at least two types of fluoropolymer

chain segments C and D containing sulfonic acid functional groups, the fluoropolymer chain segment C having a smaller equivalent weight than the fluoropolymer chain segment D.

This multi-segmented fluoropolymer is also produced by combine a segment C with a segment D in the form of blocks or a graft as shown in Fig. 1 of Appendix 1, where:

segment C : a random copolymer containing an ethylenic fluoromonomer unit containing sulfonic acid functional groups (higher content) and an ethylenic fluoromonomer unit containing no sulfonic acid functional groups.

segment D : a random copolymer containing an ethylenic fluoromonomer unit containing sulfonic acid functional groups (lower content) and an ethylenic fluoromonomer unit containing no sulfonic acid functional groups.

In the present invention, the use of the specific copolymer Segments A and B or Segments C and D in the form of blocks or a graft improves the mechanical properties, high temperature mechanical properties, heat resistance, ion conductivity, and other properties of the fluoropolymer.

Further, when the fluoropolymer is used as a material for a solid polyelectrolyte in a fuel cell, it effectively improves the heat resistance, durability, and creep resistance; and thus increasing the reliability. Masayuki discloses the use of a cation exchange membrane comprising a perfluorocarbon copolymer having sulfonic acid groups, in a solid polyelectrolyte fuel cell.

Masayuki mentions a copolymer of  $\text{CF}_2=\text{CF}_2$  and  $\text{CF}_2=\text{CF}-(\text{OCF}_2\text{CFX})_m-\text{O}_q-(\text{CF}_2)_n-\text{A}$  as a perfluorocarbon polymer, and employs a copolymer of  $\text{CF}_2=\text{CF}_2$  and  $\text{CF}_2=\text{CFOCF}_2\text{CFCF}_3\text{O}(\text{CF}_2)_2-\text{SO}_2\text{F}$  in the Examples.

Masayuki also states, in paragraph [0016], that a polymer was prepared by a method described in JP 2-88645 (a partial translation is enclosed in **Appendix 2** to this Amendment).

JP 02-88645 only describes "The fluorine-containing polymers mentioned above in the first and second films can be manufactured by various methods.", on lines 19-20 of upper right column of page 4. Thus, JP 02-88645 does not teach a specific method for preparing a polymer. In the Examples of JP 02-88645,  $(\text{NH}_4)_2\text{S}_2\text{O}_8$ , which is a radical initiator, was used to prepare a polymer, and therefore the polymer of JP 02-88645 is believed to be a random copolymer. Accordingly, the polymer used in Masayuki is also deemed to be a random copolymer.

Applicants respectfully disagree with the Examiner's allegation that "Formula 1 of Masayuki reads upon Formula 1 of the present claims". The copolymer of Masayuki only corresponds to the segment A of the present invention.

In contrast, the fluoropolymer of the present invention comprises the above mentioned specific segments A and B. Thus the present invention is quite different from the fluorine-containing random copolymer of Masayuki corresponding to only segment A of the present invention.

Furthermore, the present multi-segmented fluoropolymer is the product of the combination of segment A (a random copolymer containing an ethylenic fluoromonomer unit containing sulfonic acid functional groups and an ethylenic fluoromonomer unit

containing no sulfonic acid functional groups) with segment B (a fluoropolymer chain segment containing no sulfonic acid functional groups) to thereby obtain the claimed fluoropolymer. Masayuki teaches nothing about a copolymer having the segment A and the segment B. Further, Masayuki is completely silent with regard to a copolymer having the segment C and the segment D.

Based on the foregoing discussion, the present invention is not anticipated by Masayuki. Applicants respectfully request that the Examiner withdraw the rejection to claims 1, 5, 6, 7 and 14-16 under 35 U.S.C. § 102(b) as being anticipated by Masayuki.

Harada discloses a cation exchange membrane comprising a copolymer represented by formula (1) or (2), which is a copolymer of a tetrafluoroethylene unit and a perfluorovinyl ether unit having sulfonic acid groups on the side chain, for use in a gas diffusion electrode for a solid polyelectrolyte fuel cell.

A specific method for producing a copolymer is not disclosed, but Harada teaches a copolymer may be prepared by providing a solution or a dispersion of a perfluorosulfonic acid copolymer represented by formula (1) or (2) (see column 7, lines 42-45). NAFION SOLUTION sold by Aldrich Chemical Co. is described as an example of the solution (see column 7, lines 54-62).

By the method of Harada, it is obvious for one of ordinary skill in the art that an obtained copolymer is a random copolymer.

Further, it is apparent to one of ordinary skill in the art that the formula (1) of Harada represents that the copolymer has "k" mole tetrafluoroethylene units to 1 mole of perfluorovinyl ether unit having sulfonic acid group and that it is a random copolymer.

In addition, Figure 2.1 of Thomas A. Davis, et al, *A first course in ion permeable membranes*, The electrochemical consultancy (1997), pp. 43-44 (enclosed herewith in **Appendix 3**), indicates that the copolymer produced by random copolymerization has about 5-14.3 moles of M1 (tetrafluoroethylene unit) to 1 mole of M3 (perfluorovinyl ether unit having acetyl group) or about 2.9-5.6 moles of M1 to 1 mole of M2 (perfluorovinyl ether unit having acetyl group).

Thus, these values of M1/M3 or M1/M2 overlap to the values "k" (2.1-7.6) or "m" (3.8-9.3) of Harada. Accordingly, it is obvious that the copolymer of the formula (1) or (2) of Harada is a random copolymer.

As mentioned above, the copolymer of Harada only corresponds to the segment A of the present invention. Therefore, the Examiner's allegation that "Formula 1 of the reference reads upon Formula 1 of the present claims" is incorrect.

In contrast, the fluoropolymer of the present invention comprises the above mentioned specific segments A and B. Therefore, the present fluoropolymer is quite different from the fluorine-containing random copolymer of Harada which only corresponds to the segment A of the present invention.

Moreover, as discussed above, the claimed multi-segmented fluoropolymer is the product of the combination of segment A (a random copolymer containing an ethylenic fluoromonomer unit containing sulfonic acid functional groups and an ethylenic fluoromonomer unit containing no sulfonic acid functional groups) with segment B (a fluoropolymer chain segment containing no sulfonic acid functional groups). However, Harada teaches nothing about a copolymer having the segment A and the segment B or a copolymer having the segment C and the segment D.

Moreover, Masayuki and Harada fail to teach or suggest that the copolymer exerts excellent effects by having the segments A and the segments B or the segments C and the segments D or a block copolymer having the segment A and the segment B or segments C and segments D).

Further, it is apparent from the Table 1 and Fig. 1 in the present specification that the copolymer of the present invention which has the segment A and segment B or the segment C and the segment D (Example 3 in Table 1 and Fig. 1) exerts a significantly enhanced effect than the random copolymer of Masayuki and Harada which only correspond to the segment A of the present invention (see Comparative Example 1 = Nafion 117 in Table 1 and Fig. 1).

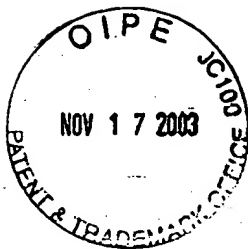
Based on the foregoing discussion, Applicants respectfully submit that the present invention is unobvious over Masayuki and Harada. Accordingly, Applicants respectfully request that the rejection to the claims under 35 U.S.C. § 103(a) be withdrawn.

Finally, by this Amendment, Applicants have corrected two clerical/typographical errors which occurred in the preparation of the present application. Specifically, Applicants have amended claim 13 from "a material according to claim 8" to "the material according to claim 8". Further, Applicants have amended claim 21 to now recite that the fluoropolymer chain segment B<sup>1</sup> is a polymer chain comprising 85 to 100 mol% from 85 to 10 mol%. Subject matter basis for the correction to claim 21 can be found in the present specification as filed on page 26, lines 19-24 and claims 6 and 35. Therefore, the correction to claim 21 does not constitute new matter.

In view of the foregoing, Applicants respectfully submit that upon entrance of the present amendment, the application will be placed in condition for immediate allowance, and entrance of the amendment and allowance of the application are respectfully requested.

**END REMARKS**





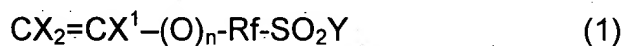
**ATTACHMENT B**  
**Amendments to the Claims**

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This listing of claims will replace all prior versions, and listings, of claims in the application.

1. (Currently Amended) A material for a solid ~~polyelectrolyte, comprising~~  
polyelectrolyte; said material comprising:  
\_\_\_\_\_ a multi-segmented fluoropolymer having; having a fluoropolymer chain segment  
A containing sulfonic acid functional groups, which is a copolymer comprising:

- (a) an ethylenic fluoromonomer unit containing sulfonic acid functional groups represented by Formula (1)



wherein X and X<sup>1</sup> may be the same or different and are each hydrogen or fluorine; Y is F, Cl or OY<sup>1</sup> wherein Y<sup>1</sup> is hydrogen, alkali metal or C<sub>1</sub> to C<sub>5</sub> alkyl; Rf is C<sub>1</sub> to C<sub>40</sub> divalent fluoroalkylene or C<sub>1</sub> to C<sub>40</sub> divalent fluoroalkylene having ether bond(s); and n is 0 or 1; and

- (b) at least one type of ethylenic fluoromonomer unit copolymerizable with the unit (a) and containing no sulfonic acid functional groups;

and a fluoropolymer chain segment B containing no sulfonic acid functional groups, the fluoropolymer chain segment B having a crystalline melting point of 100°C or higher or a glass transition point of 100°C or ~~higher~~ higher.

2-4. (Canceled)

5. (Previously presented) The material according to claim 1, wherein the at least one type of ethylenic fluoromonomer unit (b) containing no sulfonic acid functional groups comprises tetrafluoroethylene.

6. (Currently amended) The material according to claim 1, wherein the fluoropolymer chain segment B is a polymer chain comprising 85 to 100 mol% of tetrafluoroethylene and 15 to 0 mol% of a monomer represented by Formula (3)



wherein  $\text{Rf}^a$  is  $\text{CF}_3$  or  $\text{ORf}^b$  ~~wherein~~ and  $\text{Rf}^b$  is  $\text{C}_1$  to  $\text{C}_5$  perfluoroalkyl.

7. (Previously presented) The material according to claim 1, wherein the multi-segmented fluoropolymer has an equivalent weight of 400 to 1600.

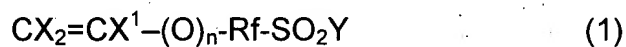
8. (Previously presented) The material according to Claim 1, comprising a multi-segmented fluoropolymer having at least two types of fluoropolymer chain segments C and D containing sulfonic acid functional groups, the fluoropolymer chain segment C having a smaller equivalent weight than the fluoropolymer chain segment D.

9. (Original) The material according to Claim 8, wherein the fluoropolymer chain segment D has a crystalline melting point of 100°C or higher or a glass transition point of 100°C or higher.

10. (Original) The material according to Claim 8, wherein the fluoropolymer chain segments C and D containing sulfonic acid functional groups are each a copolymer comprising:

- (c) an ethylenic fluoromonomer unit containing sulfonic acid function groups; and
- (d) at least one type of ethylenic fluoromonomer unit copolymerizable with the unit (c) and containing no sulfonic acid functional groups.

11. (Previously presented) The material according to claim 10, wherein the ethylenic fluoromonomer unit (c) containing sulfonic acid functional groups is represented by Formula (1)



wherein X and X<sup>1</sup> may be the same or different and are each hydrogen or fluorine; Y is F, Cl or OY<sup>1</sup> wherein Y<sup>1</sup> is hydrogen, alkali metal or C<sub>1</sub> to C<sub>5</sub> alkyl; Rf is C<sub>1</sub> to C<sub>40</sub> divalent fluoroalkylene or C<sub>1</sub> to C<sub>40</sub> divalent fluoroalkylene having ether bond(s); and n is 0 or 1.

12. (Previously presented) The material according to Claim 8, comprising the multi-segmented fluoropolymer in which the fluoropolymer chain segment D has an equivalent weight of 1000 or more.

13. (Currently Amended)—A The material according to Claim 8, wherein the multi-segmented fluoropolymer has an equivalent weight of 400 to 1600.

14. (Previously presented) A solid polyelectrolyte membrane comprising the multi-segmented fluoropolymer according to claim 1.

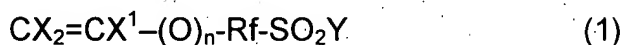
15. (Original) The solid polyelectrolyte membrane according to Claim 14, wherein the multi-segmented fluoropolymer contains protonated sulfonic acid ( $\text{SO}_3\text{H}$ ) groups as the sulfonic acid functional groups, and has a modulus of elasticity of at least  $1 \times 10^8 \text{ dyn/cm}^2$  at  $110^\circ\text{C}$  or higher.

16. (Original) The solid polyelectrolyte membrane according to Claim 15, wherein the equivalent weight of the whole multi-segmented fluoropolymer is 1600 or less.

17. (Previously presented) A multi-segmented fluoropolymer having a fluoropolymer chain segment  $\text{A}^1$  containing sulfonic acid functional groups and a fluoropolymer chain segment  $\text{B}^1$  containing no sulfonic acid functional groups, wherein:

the fluoropolymer chain segment A<sup>1</sup> containing sulfonic acid functional groups is a copolymer having a molecular weight of 5000 to 750000 and comprising:

- (e) 1 to 50 mol% of at least one type of structural unit represented by Formula (1)

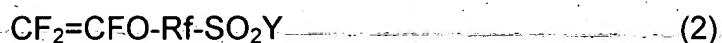


wherein X and X<sup>1</sup> may be the same or different and are each hydrogen or fluorine; Y is F, Cl and OY<sup>1</sup> wherein Y<sup>1</sup> is hydrogen, alkali metal or C<sub>1</sub> to C<sub>5</sub> alkyl; Rf is C<sub>1</sub> to C<sub>40</sub> divalent fluoroalkylene or C<sub>1</sub> to C<sub>40</sub> divalent fluoroalkylene having ether bond(s); and n is 0 or 1, and

- (f) 99 to 50 mol% of at least one type of ethylenic monomer structural unit containing no sulfonic acid functional groups; and

the fluoropolymer chain segment B<sup>1</sup> is a fluoropolymer chain containing at least one type of ethylenic fluoromonomer unit and having a molecular weight of 3000 to 12000000.

18. (Previously presented) The multi-segmented fluoropolymer according to claim 17, wherein the ethylenic fluoromonomer (e) in the fluoropolymer chain segment A<sup>1</sup> is represented by Formula (2)



wherein Y is F, Cl or OY<sup>1</sup> wherein Y<sup>1</sup> is hydrogen, alkali metal or C<sub>1</sub> to C<sub>5</sub> alkyl; Rf is C<sub>1</sub> to C<sub>40</sub> divalent fluoroalkylene or C<sub>1</sub> to C<sub>40</sub> divalent fluoroalkylene or C<sub>1</sub> to C<sub>40</sub> divalent fluoroalkylene having ether bond(s).

19. (Original) The multi-segmented fluoropolymer according to Claim 17, wherein the ethylenic monomer (f) in the fluoropolymer chain segment A<sup>1</sup> contains at least one ethylenic fluoromonomer.

20. (Original) The multi-segmented fluoropolymer according to Claim 19, wherein the ethylenic monomer (f) is tetrafluoroethylene.

21. (Currently Amended) The multi-segmented fluoropolymer according to Claim 17, wherein the fluoropolymer chain segment B<sup>1</sup> is a polymer chain comprising 85 to ~~10 mol%~~ 100 mol% of tetrafluoroethylene and 15 to 0 mol% of a monomer represented by Formula (3)

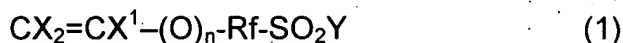


Wherein ~~wherein~~ Rf<sup>a</sup> is CF<sub>3</sub> or ORf<sup>b</sup> ~~wherein and~~ Rf<sup>b</sup> is C<sub>1</sub> to C<sub>5</sub> perfluoroalkyl.

22. (Previously presented) A multi-segmented fluoropolymer having at least two types of fluoropolymer chain segments C<sup>1</sup> and D<sup>1</sup> containing sulfonic acid functional groups, wherein:

the fluoropolymer chain segment C<sup>1</sup> is a copolymer having a molecular weight of 5000 to 750000 and comprising:

(g) 13 to 50 mol% of at least one type of ethylenic fluoromonomer structural unit containing sulfonic acid functional groups and represented in Formula (1)

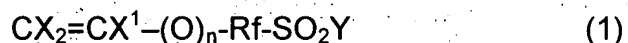


wherein X and X<sup>1</sup> may be the same or different and are each hydrogen or fluorine; Y is F, Cl or OY<sup>1</sup> wherein Y<sup>1</sup> is hydrogen, alkali metal or C<sub>1</sub> to C<sub>5</sub> alkyl; Rf is C<sub>1</sub> to C<sub>40</sub> divalent fluoroalkylene or C<sub>1</sub> to C<sub>40</sub> divalent fluoroalkylene having ether bond(s); and n is 0 or 1, and

(h) 87 to 50 mol% of at least one type of ethylenic monomer structural unit containing no sulfonic acid functional groups; and

the fluoropolymer chain segment D<sup>1</sup> is a fluoropolymer chain having a molecular weight of 3000 to 1200000 and comprising:

(i) not less than 0.1 mol% but less than 13 mol% of at least one type of ethylenic fluoromonomer unit containing sulfonic acid functional groups and represented by Formula (1)



wherein X, X<sup>1</sup>, Y, n and Rf are as defined above, and

(j) more than 87 mol% but not more than 99.9 mol% of at least one type of ethylenic monomer unit containing no sulfonic acid functional groups.

23. (Previously presented) The multi-segmented fluoropolymer according to claim 22, wherein the ethylenic fluoromonomer (g) in the fluoropolymer chain segment C<sup>1</sup> is represented by Formula (2)



wherein Y is F, Cl or OY<sup>1</sup> wherein Y<sup>1</sup> is hydrogen, alkali metal or C<sub>1</sub> to C<sub>5</sub> alkyl; Rf is C<sub>1</sub> to C<sub>40</sub> divalent fluoroalkylene or C<sub>1</sub> to C<sub>40</sub> divalent fluoroalkylene having ether bond(s).

24. (Original) The multi-segmented fluoropolymer according to Claim 22, wherein the ethylenic monomer (h) in the fluoropolymer chain segment C<sup>1</sup> contains at least one ethylenic fluoromonomer.

25. (Original) The multi-segmented fluoropolymer according to Claim 24, wherein the ethylenic monomer (h) in the fluoropolymer chain segment C<sup>1</sup> is tetrafluoroethylene.

26. (Previously presented) The multi-segmented fluoropolymer according to claim 22, wherein the ethylenic fluoromonomer (i) in the fluoropolymer chain segment D<sup>1</sup> is represented by Formula (2)



wherein Y is F, Cl or OY<sup>1</sup> wherein Y<sup>1</sup> is hydrogen, alkali metal or C<sub>1</sub> to C<sub>5</sub> alkyl; Rf is C<sub>1</sub> to C<sub>40</sub> divalent fluoroalkylene or C<sub>1</sub> to C<sub>40</sub> divalent fluoroalkylene having ether bond(s).

27. (Original) The multi-segmented fluoropolymer according to Claim 22, wherein the ethylenic monomer (j) in the fluoropolymer chain segment D<sup>1</sup> contains at least one ethylenic fluoromonomer.

28. (Original) The multi-segmented fluoropolymer according to Claim 27, wherein the ethylenic monomer (j) in the fluoropolymer chain segment D<sup>1</sup> is tetrafluoroethylene.



29. (Previously Presented) A solid polyelectrolyte membrane comprising the multi-segmented fluoropolymer according to claim 8.

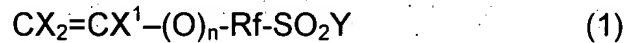
30. (Previously Presented) A material for a solid polyelectrolyte, comprising a multi-segmented fluoropolymer that comprises a block copolymer containing at least two types of fluoropolymer chain segments differing in monomer composition, at least one type of the fluoropolymer chain segments containing sulfonic acid functional groups.

31. (Previously Presented) The material according to claim 30, which comprises a multi-segmented fluoropolymer that comprises a block copolymer containing a fluoropolymer chain segment A containing sulfonic acid functional groups and a fluoropolymer chain segment B containing no sulfonic acid functional groups, the fluoropolymer chain segment B having a crystalline melting point of 100°C or higher or a glass transition point of 100°C or higher.

32. (Previously Presented) The material according to claim 31, wherein the fluoropolymer chain segment A containing sulfonic acid functional groups is a copolymer comprising:

- (a) an ethylenic fluoropolymer unit containing sulfonic acid functional groups;
- and
- (b) at least one type of ethylenic fluoromonomer unit copolymerizable with the unit (a) and containing no sulfonic acid functional groups.

33. (Previously Presented) The material according to claim 32, wherein the ethylenic fluoromonomer unit (a) containing sulfonic acid functional groups is represented by Formula (1)



wherein X and X<sup>1</sup> may be the same or different and are each hydrogen or fluorine; Y is F, Cl or OY<sup>1</sup> wherein Y<sup>1</sup> is hydrogen, alkali metal or C<sub>1</sub> to C<sub>5</sub> alkyl; Rf is C<sub>1</sub> to C<sub>40</sub> divalent fluoroalkylene or C<sub>1</sub> to C<sub>40</sub> divalent fluoroalkylene having ether bond(s); and n is 0 or 1.

34. (Previously Presented) The material according to claim 32, wherein the at least one type of ethylenic fluoromonomer unit (b) containing no sulfonic acid functional groups is tetrafluoroethylene.

35. (Previously Presented) The material according to claim 31, wherein the fluoropolymer chain segment B is a polymer chain comprising 85 to 100 mol% of tetrafluoroethylene and 15 to 0 mol% of a monomer represented by Formula (3)



wherein Rf<sup>a</sup> is CF<sub>3</sub> or ORf<sup>b</sup> wherein Rf<sup>b</sup> is C<sub>1</sub> to C<sub>5</sub> perfluoroalkyl.

36. (Previously Presented) The material according to claim 31, wherein the multi-segmented fluoropolymer has an equivalent weight of 400 to 1600.

37. (Currently Amended) The material according to claim 8, which comprises a multi-segmented fluoropolymer having a block copolymer of at least two types of fluoropolymer chain segments C and D containing sulfonic acid functional groups, the fluoropolymer chain-segment ~~D~~ segment C having a smaller equivalent weight than the fluoropolymer chain segment D.

38. (Previously Presented) A solid polyelectrolyte membrane comprising the multi-segmented fluoropolymer according to claim 30.

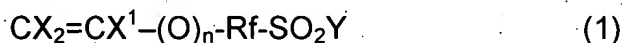
39. (Previously Presented) The solid polyelectrolyte membrane according to claim 38, wherein the multi-segmented fluoropolymer contains protonated sulfonic acid ( $\text{SO}_3\text{H}$ ) groups as the sulfonic acid functional groups, and has a modulus of elasticity of at least  $1 \times 10^8$  dyn/cm<sup>2</sup> at 110°C or higher.

40. (Previously Presented) The solid polyelectrolyte membrane according to claim 39, wherein the equivalent weight of the whole multi-segmented fluoropolymer is 1600 or less.

41. (Previously Presented) The multi-segmented fluoropolymer according to claim 17, which has a block copolymer of a fluoropolymer chain segment A<sup>1</sup> containing sulfonic acid functional groups and a fluoropolymer chain segment B<sup>1</sup> containing no sulfonic acid functional groups, wherein:

the fluoropolymer chain segment A<sup>1</sup> containing sulfonic acid functional groups is a copolymer having a molecular weight of 5000 to 750000 and comprising:

- (e) 1 to 50 mol% of at least one type of structural unit represented by Formula (1).



wherein X and X<sup>1</sup> may be the same or different and are each hydrogen or fluorine; Y is F, Cl or OY<sup>1</sup> wherein Y<sup>1</sup> is hydrogen, alkali metal or C<sub>1</sub> to C<sub>5</sub> alkyl; Rf is C<sub>1</sub> to C<sub>40</sub> divalent fluoroalkylene or C<sub>1</sub> to C<sub>40</sub> divalent fluoroalkylene having ether bond(s); and n is 0 or 1, and,

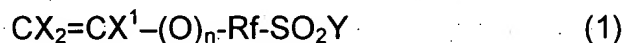
- (f) 99 to 50 mol% of at least one type of ethylenic monomer structural unit containing no sulfonic acid functional groups; and

the fluoropolymer chain segment B<sup>1</sup> is a fluoropolymer chain containing at least one type of ethylenic fluoromonomer unit and having a molecular weight of 3000 to 1200000.

42. (Previously Presented) The multi-segmented fluoropolymer according to claim 22, which has a block copolymer of at least two types of fluoropolymer chain segments C<sup>1</sup> and D<sup>1</sup> containing sulfonic acid functional groups, wherein:

the fluoropolymer chain segment C<sup>1</sup> is a copolymer having a molecular weight of 5000 to 750000 and comprising:

- (g) 13 to 50 mol% of at least one type of ethylenic fluoromonomer structural unit containing sulfonic acid functional groups and represented by Formula (1).

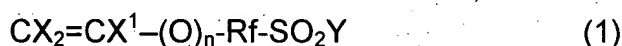


wherein X and X<sup>1</sup> may be the same or different and are each hydrogen or fluorine; Y is F, Cl or OY<sup>1</sup> wherein Y<sup>1</sup> is hydrogen, alkali metal or C<sub>1</sub> to C<sub>40</sub> divalent fluoroalkylene having ether bond(s); and n is 0 or 1, and

(h) 87 to 50 mol% of at least one type of ethylenic monomer structural unit containing no sulfonic acid functional groups; and

the fluoropolymer chain segment D<sup>1</sup> is a fluoropolymer chain having a molecular weight of 3000 to 1200000 and comprising:

(i) not less than 0.1 mol% but less than 13 mol% of at least one type of ethylenic fluoromonomer unit containing sulfonic acid functional groups and represented by Formula (a)

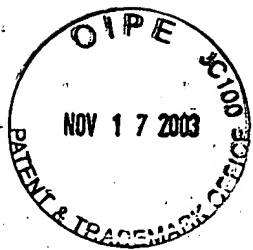


wherein X, X<sup>1</sup>, Y, n and Rf are as defined above, and

(j) more than 87 mol% but not more than 99.9 mol% of at least one type of ethylenic monomer unit containing no sulfonic acid functional groups.

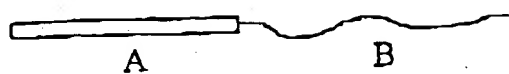
43. (Previously Presented) The solid polyelectrolyte membrane according to claim 29, wherein the multi-segments fluoropolymer contains protonated sulfonic acid (SO<sub>3</sub>H) groups as the sulfonic acid functional groups, and has a modulus of elasticity of at least 1X10<sup>8</sup> dyn/cm<sup>2</sup> at 110°C or higher.

44. (Previously Presented) The solid polyelectrolyte membrane according to claim 43, wherein the equivalent weight of the whole multi-segmented fluoropolymer is 1600 or less.



# APPENDIX 1

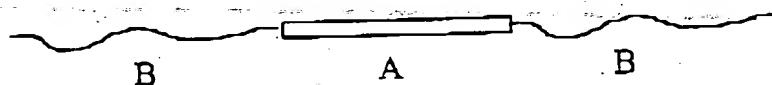
Copy of Fig. 1 From The Present Specification



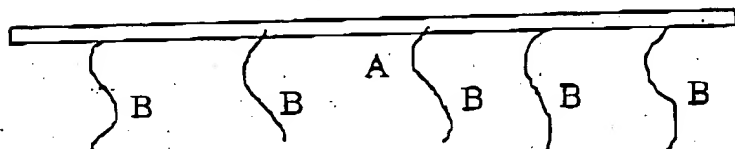
A-B block copolymer



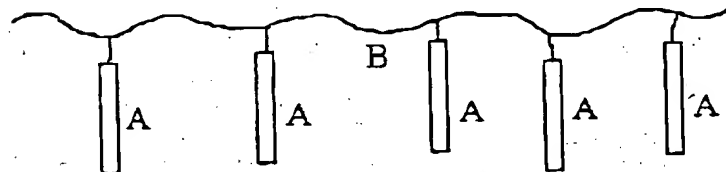
A-B-A block copolymer



B-A-B block copolymer

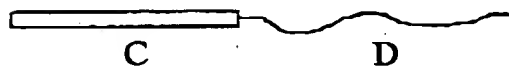


A-B graft copolymer



B-A graft copolymer

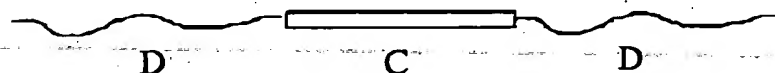
< Reference Figure >



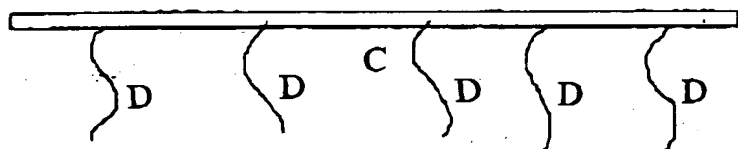
C-D block copolymer



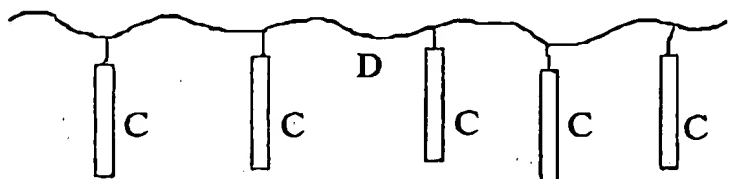
C-D-C block copolymer



D-C-D block copolymer



C-D graft copolymer



D-C graft copolymer

## APPENDIX 2

< Partial translation of Japanese Unexamined Patent  
Publication No. 02-88645 >

p.4, upper right column, lines 19-20

5           The fluorine-containing polymers mentioned above in  
the first and second films can be manufactured by various  
methods.

p.5, lower left column, line 8 to lower right column, line 6

10   [Examples]

Example 1

          In a pressure-resistant reaction vessel having a  
capacity of 10 liters were placed 6500 g of ion-exchanged water,  
13 g  $C_8F_{17}COONH_4$ , 32.3 g  $Na_2HPO_4 \cdot 12H_2O$ , 18.9 g  $NaH_2PO_4 \cdot 2H_2O$ , 5.14  
15 g  $(NH_4)_2S_2O_8$  and 0.39 g n-hexane. Then, 984 g  $CF_2=CFO(CF_2)_3COOCH_3$   
and 316 g  $CF_2=CFOC_3F_7$  were placed therein. Deaeration was  
conducted to a sufficient degree, temperature in the vessel  
was raised to 57°C, which is the polymerization temperature,  
the pressure in the vessel was raised by tetrafluoroethylene  
20 to the predetermined level, i.e., 11.7 kg/cm<sup>2</sup>, and the reaction  
was conducted. Polymerization was conducted with the  
introduction of tetrafluoroethylene thereto while maintaining  
the predetermined pressure. After 5 hours, the reaction was  
stopped, and the obtained latex was aggregated using  
25 concentrated sulfuric acid. Thereafter, the polymer was

sufficiently washed with water, treated in methanol at 65° C for 16 hours and dried, obtaining 1.42 kg of ternary copolymer having ion exchange capacity of 1.01 meq/g. The resultant ternary copolymer was extruded at 220° C, obtaining a thin film

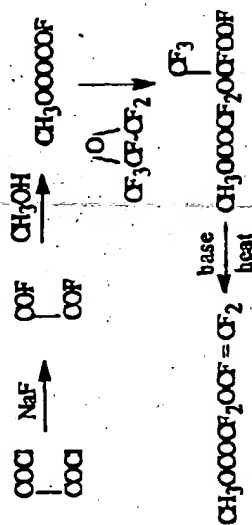
5 having a thickness of 20  $\mu$ m.



hexafluoropropylene oxide followed by heating in the presence of sodium carbonate leads to the desired monomer. The Dow monomer with  $p = 0$  and  $q = 2$  is manufactured by the same route with the modification described above for the sulfonyl fluoride monomer, i.e. 3-chloropentafluoropropylene oxide is used rather than hexafluoropropylene oxide.

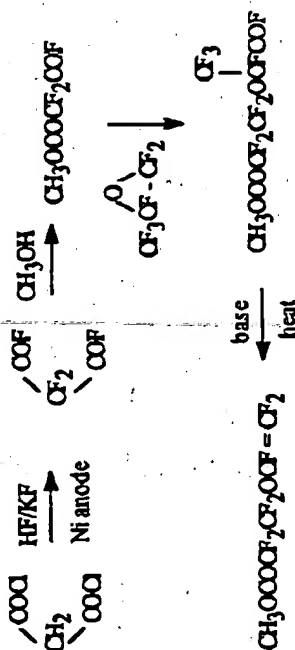
The Japanese companies have also indicated the possibility of using polymers with some of the monomers with  $p = 0$  or 1 and  $q = 1$  or 4. The monomers with  $q = 1$  are synthesised from oxalyl chloride, see scheme 10; halide exchange is followed by partial methanolysis, addition of hexafluoropropylene oxide and formation of the double bond.

Scheme 10



It is claimed that the monomers with  $q = 2, 4$  can be made by a route where the first step is the anodic perfluorination of an acid chloride of a dicarboxylic acid. For example, the monomer with  $q = 2$  is synthesised from malonyl chloride, see scheme 11.

Scheme 11



## 2.1.2 The Polymerisation Stage

The copolymerisation of tetrafluoroethylene with the substituted monomer is carried out by radical initiated polymerisation in either aqueous or non-aqueous media. Non-aqueous polymerisation is carried out in an inert halogenated solvent (possible choices include 1,1,2-trichloro-1,2,2-trifluoroethane, perfluoromethyl-cyclohexane, perfluorooctane or hexafluorobenzene) with a soluble free radical initiator such as perfluorocarboxylic acid peroxide ( $R_4\text{COO}$ ), azobis-isobutyronitrile or a fluorine radical initiator (eg.  $\text{N}_2\text{F}_2$ ). The alternative aqueous procedures employ emulsion or suspension polymerisation. In emulsion polymerisation, the monomers are present as a second phase and they are stirred with the aqueous medium containing a water soluble initiator (eg. ammonium persulfate) and an emulsifier (ammonium perfluorooctanoate) so the polymer is formed as a particle slurry. In suspension polymerisation, the reaction is again carried out in a two phase system but the initiator is soluble in the monomer and the system also contains a dispersion stabiliser. The final stage is precipitation of the polymer. The initiators are those also used in non-aqueous polymerisation.

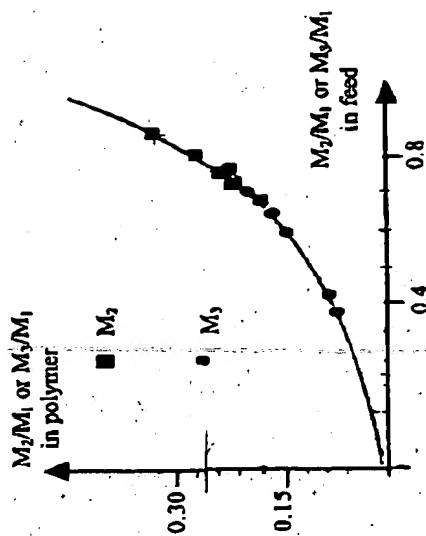


Figure 2.1 The dependence of the copolymer composition on the ratio of the monomers,  $M_1 = \text{CF}_2=\text{CF}_2$ ,  $M_2 = \text{CF}_2=\text{CFCF}_2\text{CF}_2\text{COOCH}_3$ , and  $M_3 = \text{CF}_2=\text{CFCF}_2\text{CF}_2\text{COOCH}_3$ , in the feedstock to an emulsion polymerisation [3].

Problems in the melt fabrication process can arise from the end groups resulting from the initiator; in such cases, it is necessary to carry out chemistry to modify these groups. For example, terminal carboxylate groups are not very stable when heated and hence it is common to convert them into methyl or trifluoromethyl esters.

The molecular weight of the copolymer should be high enough to obtain the required physical strength, and values may be up to  $10^6$  daltons. In practice, the molecular weight is controlled using parameters such as the temperature (which determines the half life of the initiator) and the pressure as well as the medium and the concentration of the initiator. Typically, temperatures and pressures are within the ranges 330 - 350 K and 5 - 20 atmospheres respectively. The composition of the copolymer, i.e. the equivalent weight is determined by the ratio of the two monomers. The substituted monomers react with radicals more slowly than tetrafluoroethylene and the dependence of the polymer composition on the ratio of the monomers in the feed must be determined empirically. Figure 2.1 illustrates such data.

### 2.1.3 Membrane Fabrication

From the viewpoint of processing the polymers into membranes, the sulfonyl fluoride and methyl carboxylate polymers have much superior properties to the ionic polymers formed after hydrolysis. Hence these precursors are always converted to the final membrane form before hydrolysis. All the sulfonyl fluoride and methyl carboxylate polymers whose syntheses are described above are stable to temperatures > 550 K and are melt processable; hence, they can be formed into membranes by conventional moulding and extrusion techniques. Extrusion is the preferred method for continuous production of large area of membrane material because the thickness may be more closely controlled. The conditions during the extrusion process are also believed to influence the chemical properties of the membranes. Most commercial membranes have thicknesses in the range 100 - 1000  $\mu\text{m}$  while many are reinforced with a fine polymer mesh or PTFE fabric to allow them to be easily handled without damage. Such meshes and fabrics are incorporated during the extrusion stage.

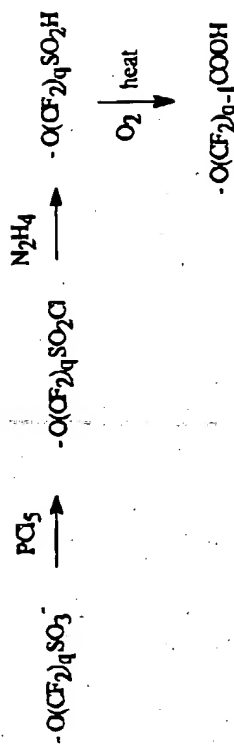
It is also common to manufacture membranes from different materials using lamination with a roll press or co-extrusion. Such techniques are used to manufacture membranes with several layers of polymer which differ in equivalent weights. It is also one approach to the manufacture of the modern chlor-alkali membranes where there is a thin layer of a carboxylate polymer on the cathode side of a sulfonic acid membrane.

### 2.1.4 Chemical Modification of the Membranes

It was noted above that the membranes are manufactured using polymers where the functional groups are precursors to the ion exchange centres. Hence, the films must be hydrolysed to give the final product. For example, the methyl ester polymer films are converted to carboxylate membranes by treatment with 25% sodium hydroxide at 360 K for 12 - 24 hours. The cations in the membrane can then be readily exchanged by soaking for a few hours in a solution of an appropriate salt. The membranes are often stored wet and in a preferred cationic form (usually  $\text{H}^+$ ,  $\text{Na}^+$  or  $\text{K}^+$ ).

Sulfonate/carboxylate layered membranes are also produced by the chemical conversion of sulfonate to carboxylate groups after the membrane has been fabricated. This can be achieved in a number of ways and one preferred method is shown in scheme 12.

Scheme 12



One surface of the sulfonate membrane in the acid form is treated with the a solution of phosphorus pentachloride to form the sulfonyl chloride which is then reduced to a sulfonic acid with a solution of hydrazine. The perfluorosulfonic acids are rather unstable and readily lose sulfur dioxide to give the carboxylic acid where the fluorocarbon chain has one less carbon than initial sulfonate polymer. This final stage can be achieved with mild oxidising agents or even oxygen with gentle heating. The depth of the chemical conversion is controlled via the reaction time, temperature and concentration of reagents. In commercial membranes, the carboxylate layer is normally thin and the conversion is limited to 10 - 20  $\mu\text{m}$ . In addition, the same parameters may be used to determine the gradient of the carboxylic acid group content at the interface with the sulfonate polymer. This